Agnostic Compact Demilitarization of Chemical Agents

ACDC

PRESENTED BY: Mr. Darrel Johnston Program Manager, Southwest Research Institute

MODERATED BY: Steve Redifer 2020-10-01



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Mr. Darrel Johnston



Southwest Research Institute

October 1, 2020

SwRI acknowledges and is profoundly thankful for funding from the Defense Advanced Research Projects Agency, DARPA, and for the independent testing support of U.S. Army Combat Capabilities Development Command (CCDC) Chemical Biological Center (CBC)

This research was developed with funding from the Defense Advanced Research Projects Agency (DARPA). The views, opinions and/or findings expressed are those of the author and should not be interpreted as representing the official views or policies of the Department of Defense or the U.S. Government.

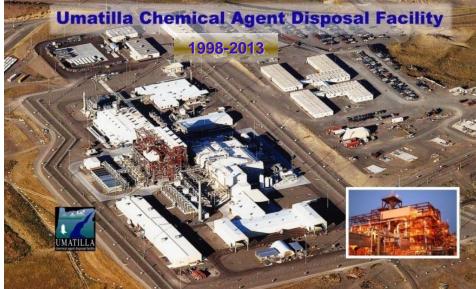
SwRI Chemical Warfare Agent Defeat/Disposal History Prior to ACDC





SwRI San Antonio CWA program dates back to 1985





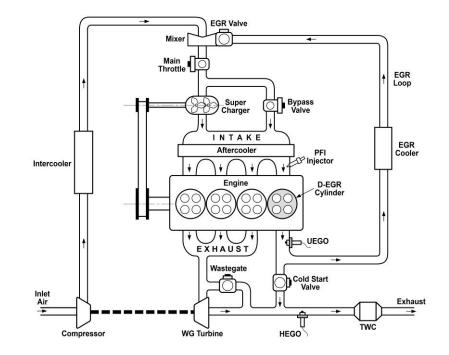






- Vehicle conversion to demonstrate SwRI Dedicated Exhaust Gas Recirculation D-EGR[®] technology
- Operational in 9 months







Syria Stockpile and Cape Ray Mission Success Inspiration for DARPA ACDC



Huge success

- 2014
- Two Field Deployable Hydrolysis System (FDHS) units
- Processed 600 tons of chemical agents¹
- DF (a sarin gas precursor)
- HD sulfur mustard

Challenges

- Logistics: Destroying bulk stores of Chemical Warfare Agents (CWAs) and their organic precursors abroad is a significant challenge for the international community
- Waste 6000 tons of chemical aqueous and solid waste²



NEWS STORIES

DoD Mobile Chemical-agent Destruction System Wins U.K. Award

A United Kingdom organization has given an innovation award to the Defense Department team responsible for developing and operating the field-deployable hydrolysis systems used aboard the U.S. ship MV Cape Ray this year to destroy tons of Syrian chemical materials. Story

Hagel Congratulates Cape Ray for Syria Mission

Defense Secretary Chuck Hagel congratulated the crew of the MV Cape Ray for completing the neutralization of Syrian chemical weapons. Story

Cape Ray Crew Destroys 75 Percent of Materials

More than 70 percent of the chemical weapons materials taken out of Syria have now been destroyed aboard the U.S. ship MV Cape Ray. Story

DoD: Progress Made in Neutralizing Materials

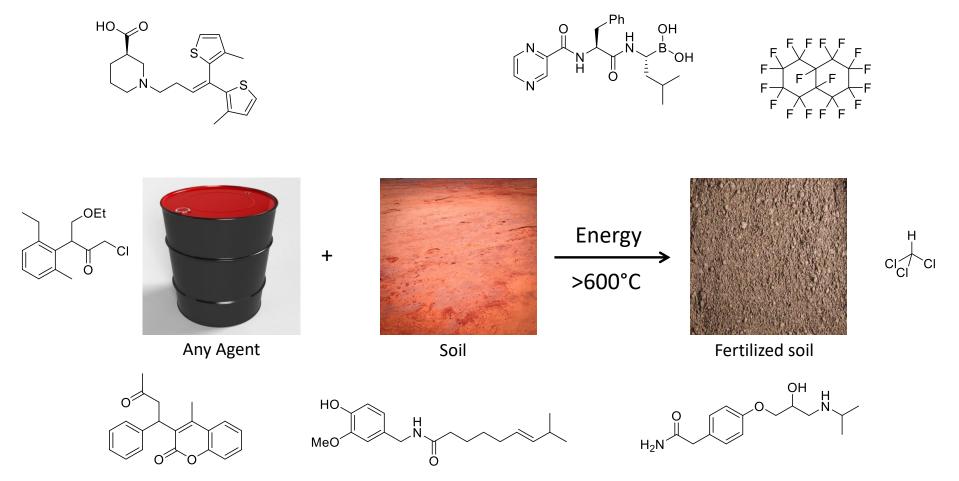
A Pentagon spokesman said teams aboard the U.S. ship MV Cape Ray are making more progress in neutralizing materials from Syria's

NEWS PHOTOS



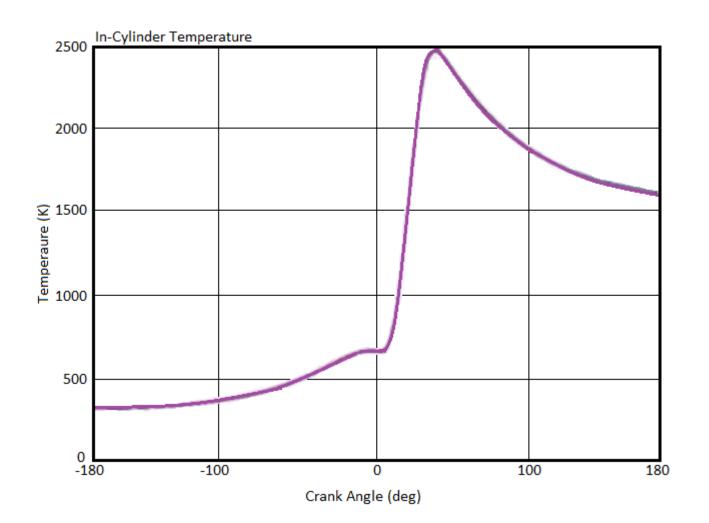
¹<u>http://mebaunion.org/M.E.B.A. Telex Times for August-21-2014.pdf</u> ²<u>https://robindesbois.org/en/le-cape-ray-arrive-en-europe-du-nord-2/</u> https://archive.defense.gov/home/features/2014/0114_caperay/

Agnostic Compact Demilitarization of Chemical Agents (ACDC) Original Vision (Dr. Tyler McQuade, DARPA, December 2014)



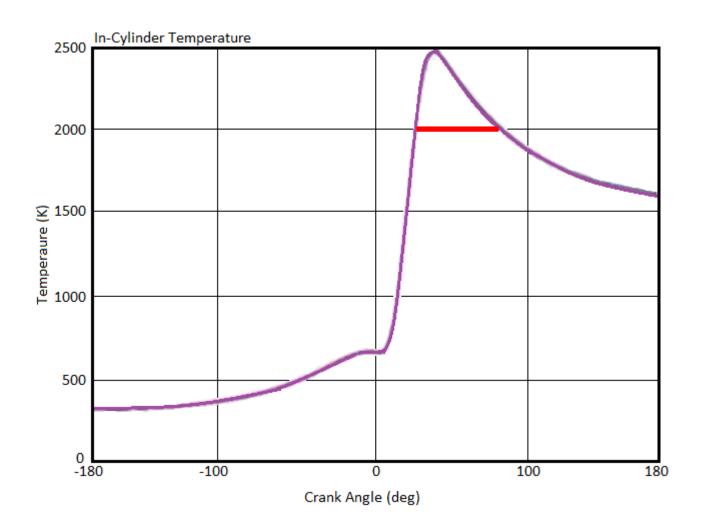
Soil/earth is a readily available worldwide resource composed of main group elements, metal salts, and metal oxides that can scavenge acids, yielding salts and compounds typically associated with fertilizer.

Engine bulk gas temperature (K) as a function of crank angle degree



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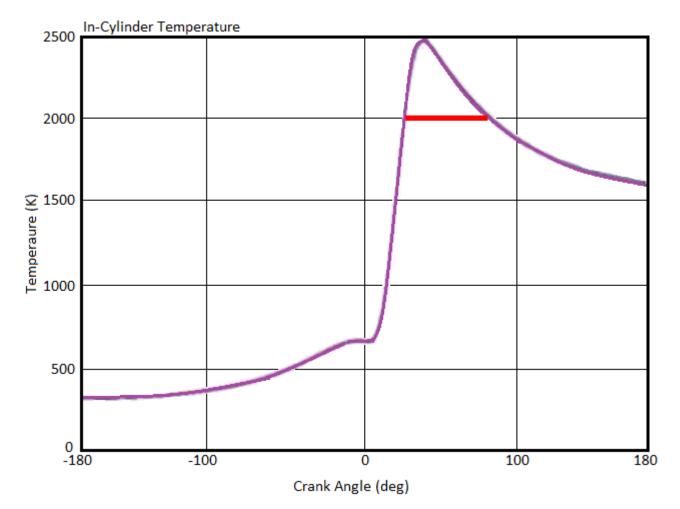
Engine bulk gas temperature (K) as a function of crank angle degree



- Decomposition rate constants for VX, HD, GB and several simulants are known
- 99.9999% conversion occurs in 20 half-lives
- Agent half-life calculations at 2000 K, fuel, air, engine speed, volume, and heat analysis, we expect to achieve greater than 10,000 half-life conversions in the cylinder

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Engine bulk gas temperature (K) as a function of crank angle degree



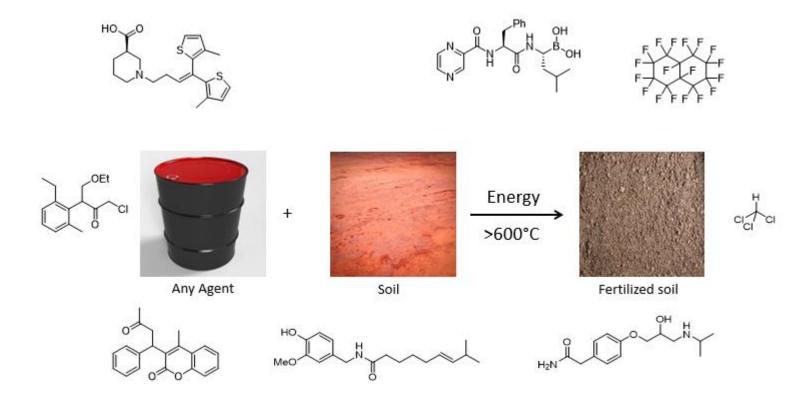
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 $2 \text{ C-H}_2 + 3 \text{ O}_2 \rightarrow 2 \text{ CO}_2 + 2 \text{ H}_2\text{O}$ $2 \text{ C-F} + \text{H}_2 + 2 \text{ O}_2 \rightarrow 2 \text{ HF} + 2 \text{ CO}_2$ $2 \text{ C-CI} + \text{H}_2 + 2 \text{ O}_2 \rightarrow 2 \text{ HCI} + 2 \text{ CO}_2$ $4 \text{ C-P} + 9 \text{ O}_2 \rightarrow 2 \text{ P}_2\text{O}_5 + 4 \text{ CO}_2 \text{ (+ other acids of P)}$ $\text{C-S} + 2 \text{ O}_2 \rightarrow \text{SO}_2 + \text{ CO}_2 \text{ (+ acids of sulfur)}$ $\text{C-N} + \text{ O}_2 \rightarrow \text{ oxides of nitrogen (N_2\text{O}, \text{ NO}, \text{ NO}_2) + \text{ CO}_2$ **Calciferous Soil Should Adsorb Acid Gases**



ACDC Proof-of-principle demonstrations

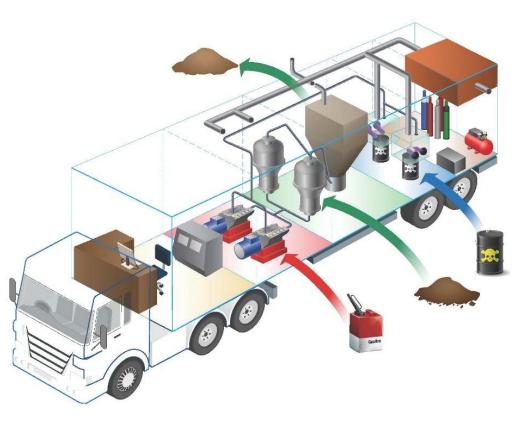
• Dec '14 – DARPA goal to destroy Syria-sized stockpile with indigenous materials (e.g., soil)





ACDC Proof-of-principle demonstrations

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- Sep '15 Contract Award to SwRI: gasoline engine + soil-based gas scrubber

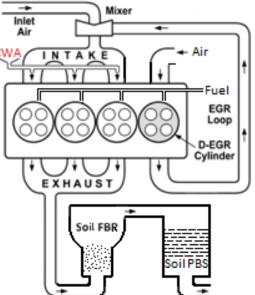




ACDC Proof-of-principle demonstrations

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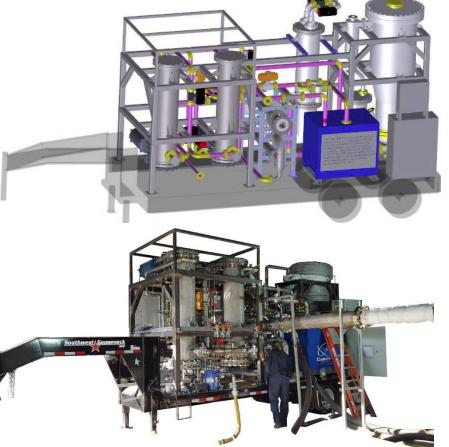






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 - Diesel engine (gasoline engine was knock limited)
 - Polyphosphoric acid drop-out needed for organophosphate agents



SwRI

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Development of Expeditionary Destruction System (EXDS)

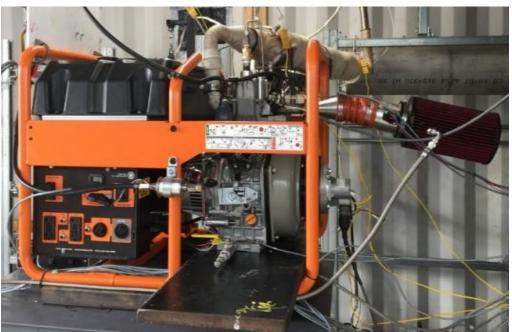
- Nov '17 DARPA goal revised to expedient 'get-in, get-out' mission
- Feb '18 End user goals established and potential user selected vehicle
- Dec '18 SwRI obtained truck and spare engine
 - OEM engine modified to include addition of stock superchargers and replacing engine valves and seats to more chemical resistant materials
 - Manufactured and integrated novel ammonia-based pollution control system (PAS)
- Apr '19 Simulant testing of modified engine on test stand
- Oct '19 Simulant testing of truck-mounted engine and acid gas scrubber
- Nov '19 Simulant testing of EXDS concluded at SwRI
- Dec '19 EXDS shipped to US Government facility for validation testing (CCDC APGEA)
- Feb '20 Simulant testing demonstrated DRE between 99.9988% and 99.9995% destruction and Removal Efficiency (DRE) of HD-simulant and 99.94% removal of acid gas from exhaust



Early-stage concept validation for diesel engine as CWA treatment



- 435 cc Diesel engine Proof of Concept in 2017:
- 99.5% DRE on TFA & TEP simulants
- Not knock-limited
- 1 L in 15 minutes, 4 L/hr rate
- ~10 LPH per Liter Engine Displacement rule of thumb



CWA	Simulant
Sarin (GB)	Trifluoroacetic acid (TFA) + Triethyl phosphate (TEP)
VX	Diisopropylamine (DIPA) + Diethylphosphite (DEPi) + Thiophene (TP)

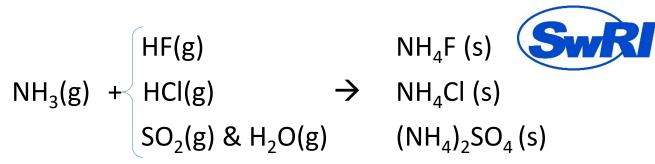
Based on these results, DARPA held a potential user meeting in February 2018 to define mission-specific metrics on which a first-generation diesel-based prototype system could be built

Tactical: Drive-in, Drive-out

- End User Set Specs
- Trade Space Parameters
 - Engine
 - Power dissipation
 - Scrubber
 - Vehicle load limits
- Best Solution
 - Modern 4.5L V8 diesel
 - Power dissipation: Supercharger(s)
 - Scrubber: Ammonia
 - Vehicle: Pickup Truck

	Pickup	Pickup	Pickup
	4.5L V8 diesel	4L diesel	3L I4 turbo diesel
	common rail	mechanical	common rail
	injection	injection	injection
ikelihood to achieve required DRE	Likely	Un-likely	Likely
Ouration of mission	10.5 hours	11.2 hours	15.1 hours
Acid Gas Scrubber			
Stack Only	Base option	Base option	Base option
Packed Tower Scrubber	over vehicle load	over vehicle load	over vehicle load
	rating by >2x	rating by >2x	rating by >5x
Packed Bed Scrubber	over vehicle load	over vehicle load	over vehicle load
	rating by >4x	rating by >4x	rating by >9x
Liquid Venturi Scrubber	over vehicle load	over vehicle load	over vehicle load
	rating by >2x	rating by >2x	rating by >5x
Single Pass Dry Injection	over vehicle load	over vehicle load	over vehicle load
	rating by >2x	rating by >2x	rating by >3x
Re-Use Dry Injection	over vehicle load	over vehicle load	over vehicle load
	rating	rating	rating by >2x
Ammonia	fits within vehicle	fits within vehicle	over vehicle load
	load rating	load rating	rating
ant "A" (Approved for Dublic Delease, Distribution Unlimited)			

Ultralight Scrubber



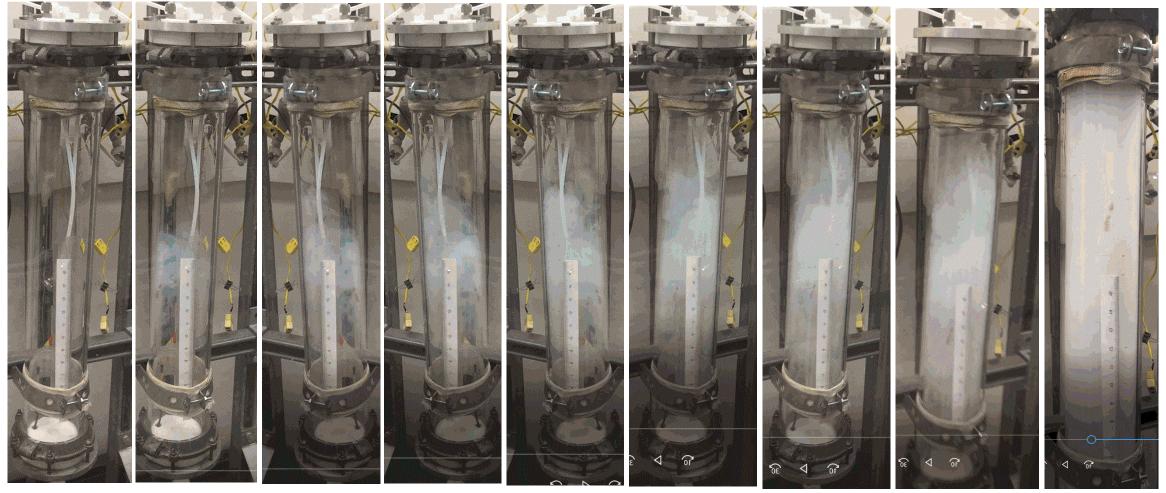
- Reviewed all known acid scrubbing methods
- Scrubbing efficiency and capacity versus weight considerations
 - Eliminated Transportable Solid Scrubber Options
 - Eliminated Aqueous Scrubber Options
 - Favored Gaseous Scrubbing with Ammonia (NH₃)
- Sources of NH_3 considered
 - Anhydrous compressed cylinder
 - Solid urea, ammonium carbonate, ammonium carbamate
 - Sequestered ammonia in metal-chloride matrix (e.g., LiCl·4NH₃)
 - Concentrated aqueous ammonium hydroxide with spray aspiration
- Aqueous NH₄OH gave best efficiency, with lowest weight and system complexity

Bench-scale NH₃ Scrubber Proof of Concept Test

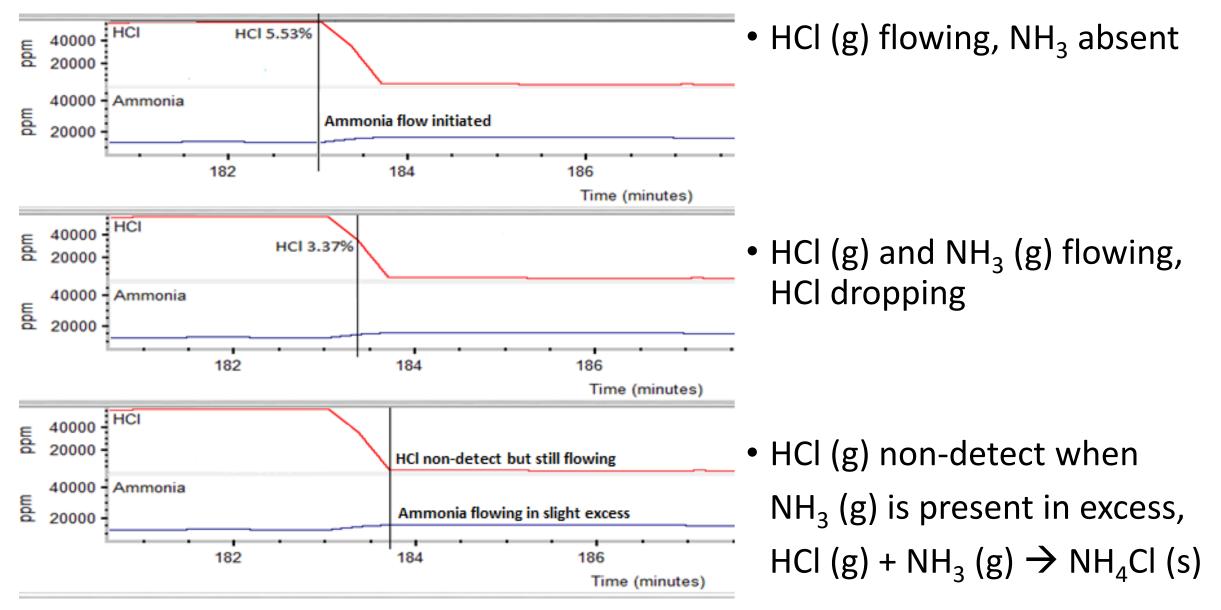


- HCl + NH₃ at 1-second time increments
- Also tested $SO_2 + NH_3 + H_2O$

- Monitored Temp and Pressure
- FTIR monitoring for acid gases

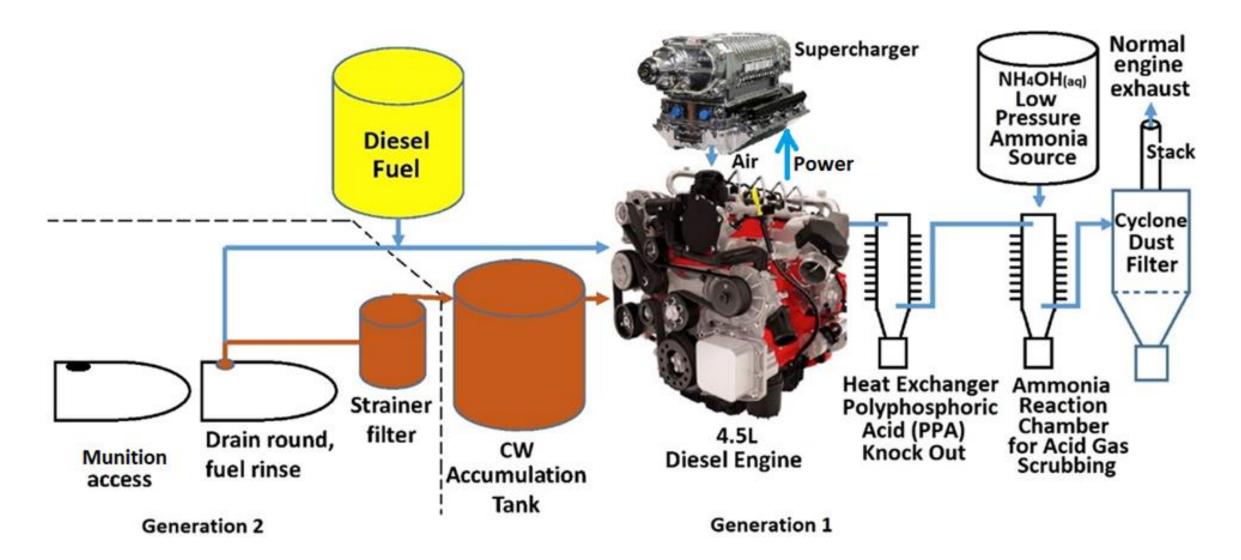


FTIR Trace of HCl and Ammonia Interaction



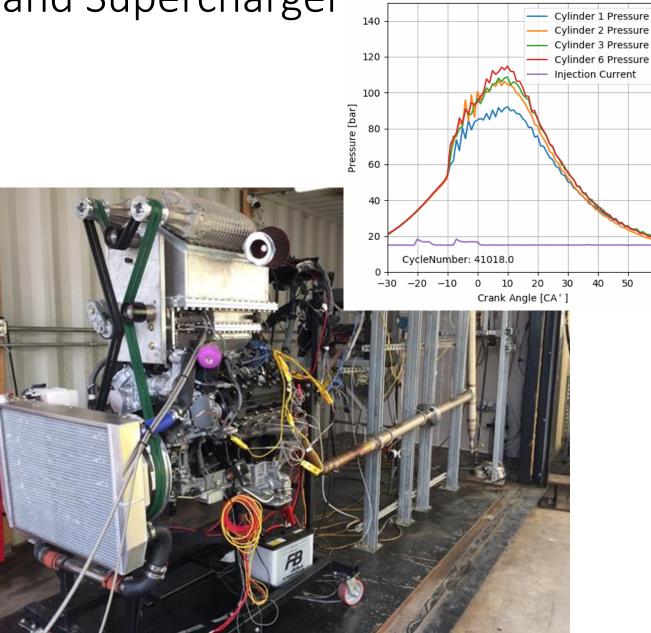
Process Flow





Proof of Concept 4.5 L Engine and Supercharger

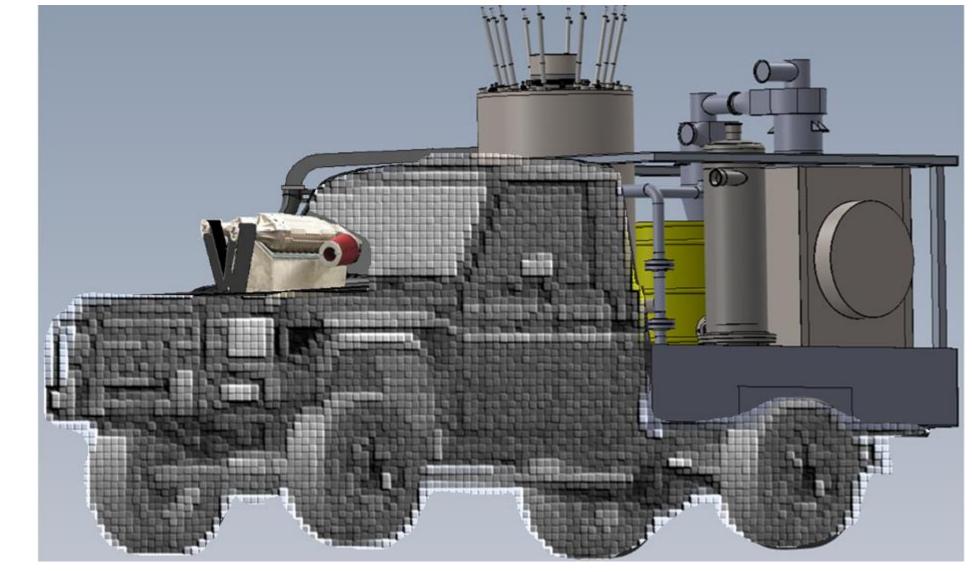
- Modified Engine
 - Inconel Valves
 - Nickeloy Seats
 - Gapless Rings
 - Pressure Transducers in Cylinders
 - Two superchargers
- Demonstrated:
 - Simulant destruction >99.999%
 - Power dissipation : Superchargers
- Air Uses:
 - Supercharge the engine
 - NH₄OH(aq) nozzle atomization
 - Dilution cooling of exhaust



Expeditionary Destruction System (EXDS) - Design

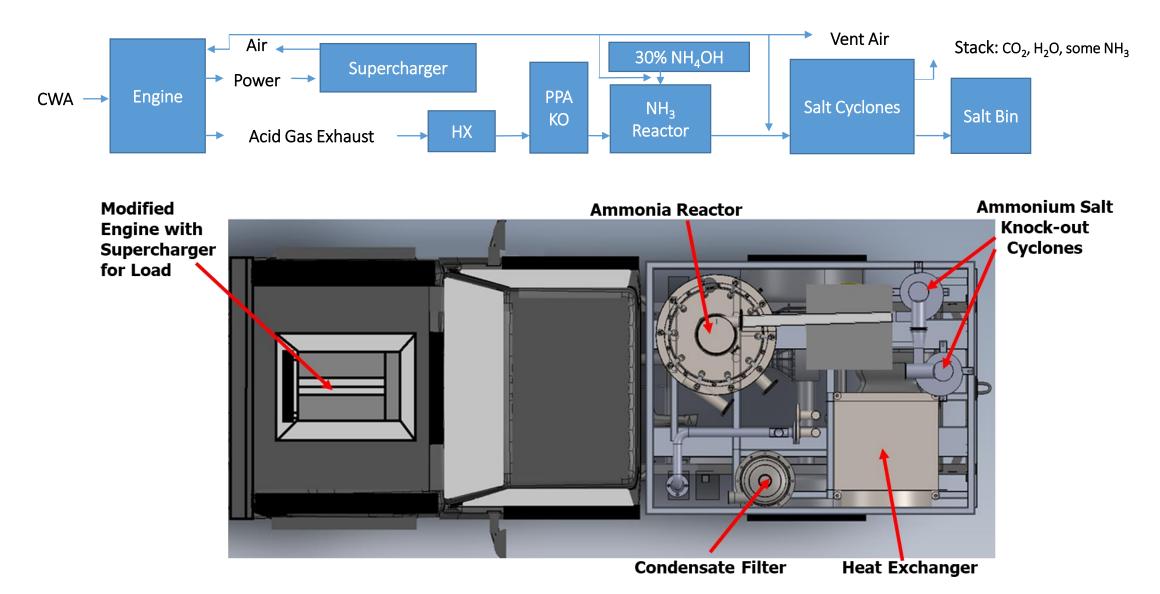


- Integrate systems into vehicle
- Engine
- Superchargers
- Ammonia Scrubber



EXDS System and Subsystems





EXDS Scrubber Build

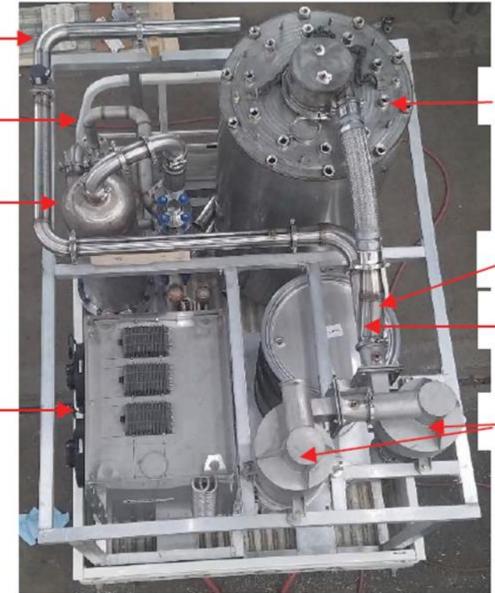


Air from superchargers-

Engine exhaust coming in

2. PPA knockout cyclone-

1. Heat exchanger (HX)



- 3. Ammonia reactor

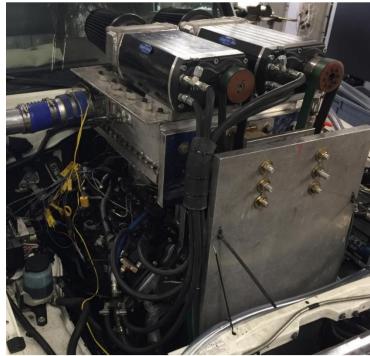
Ammonium hydroxide tank

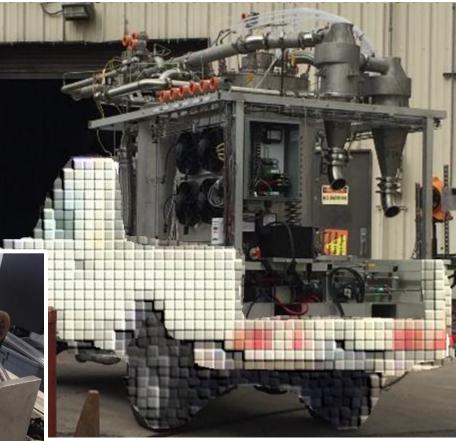
-4. Cooling air union

= 5. Ammonium salt cyclones

EXDS – Key Features (Generation 1 prototype)

- Modified diesel engine that burns CWA as fuel
- Acid gas scrubber to capture CWA decomposition products
- Operational Concept: Drive in, Destroy CWA, Drive out
- Technology scalable to multiple operational scenarios
- Numerous vehicle options
- Straightforward operation
- Minimal logistical/environment impacts





EXDS Test Program

SwRI Test Results

- 315 L Simulant destroyed
 - Diisopropylamine (DIPA) + Diethylphosphite (DEPi) + 1,1,1-Tetrahydrothiophene (TP)
 - GB: Trifluoroacetic acid (TFA) + Triethyl phosphate (TEP)
 - HD: 1,2,4-trichlorobenzene (TCB) and TP
- DRE consistently >99.99%
- Acid gases, HCl & SO₂ removed >99%, made Ammonium Salts
- Feed rate equivalent to heating value of HD at 35 L/hr (55 gallons/6 hours)
- Capacity
 - Limiting reagent: ammonia, 55 gal 30% NH₄OH per 100 L HD
 - Prototype system built to carry one 55-gal drum ammonia

Demonstration Results

- IV&V: CCDC test facility; CCDC-DAC test report
- 50/50 molar mix of 1,4-dichlorobutane (DCB) and dibutylsulfide (DBS).
- Demonstrated Simulant DRE between 99.9988% and 99.9995% before acid gas scrubber
- HCl removed to non-detect, SO₂ removed to 99.94%





Testing with Authentic CWA Not Undertaken

- Testing with CWA-simulant was successful with 315 L at SwRI and 23 L at CCDC
- Testing with authentic CWA was not initiated
- Weak link was acid gas scrubber, 316 SS
- Metal gages were thin for weight trade-off
- Acid gases pitted scrubber components faster than predicted
- Gas leaks through scrubber components ended testing



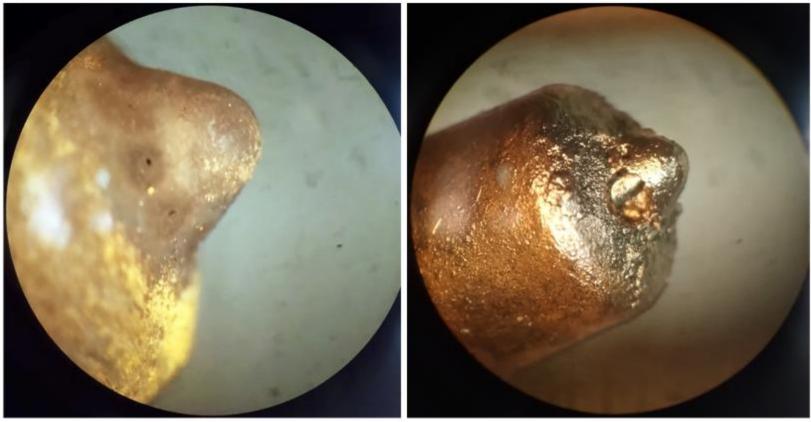


Evaluation of Engine After Simulant Testing



Injectors

- Tips of four injectors were compromised from outside-in by corrosion
- Future engines will need more acid-resistant injectors and/or acid-resistant coatings



Normal

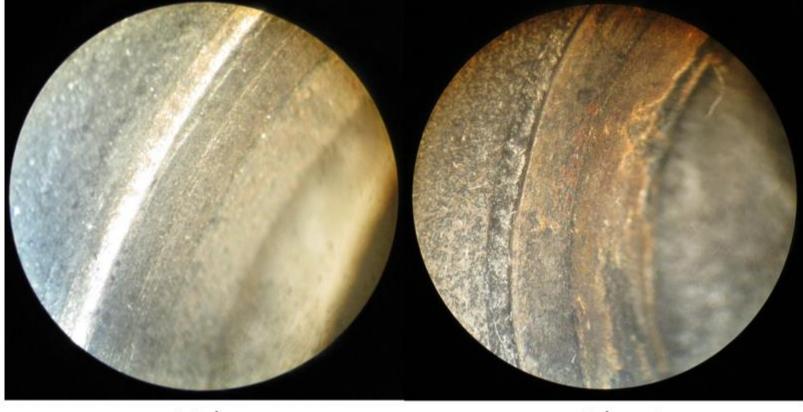
Damaged

Evaluation of Engine After Simulant Testing



Valves

• Valves (Inconel) and valve seats (Nickeloy) functioned well and sealed well throughout 214.6 L testing



Rings

Intake

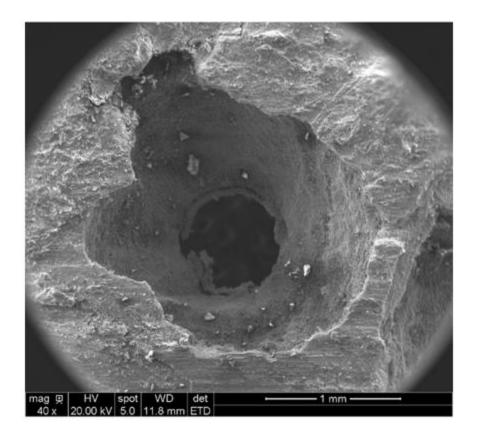


• Normal deposits, cylinder walls appeared normal



Evaluation of Ammonia Scrubber After Testing

- Through wall leaks in Heat Exchanger and Ammonia Scrubber
 - Typical of acid-metal corrosion
 - Avoidable with acid-resistant alloys or coatings
 - Increased Cr, Ni, and Mo enhance the resistance to pitting
 - Hastelloy C-2000 and Hastelloy C-276



Micrograph of Ammonia Reactor Through Wall Leak

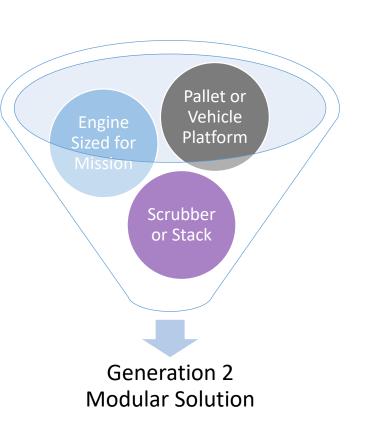
Generation 2

Generation 2 Upgrades

- Scrubber system materials Hastelloy or other acid-resistant alloy or coatings
- Injector acid-resistant alloy or coatings
- Interface with COTS munitions access, CWA filtration, agent tank
- Simpler user interface and automated operation

End-user driven Gen 2 concept

- Needs an end-user transition partner to proceed
- System configuration dictated by scale and duration of mission
- Drive-in, drive-out versus cargo configuration







Question & Answer

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DARPA Point of Contact: Dr. Anne Fischer, DARPA Defense Sciences Office Program Manager Email: Anne.Fischer@darpa.mil Phone: 703-526-2831

CCDC CBC Point of Contact: Raymond DiBerardo, EXDS Project Manager Office Symbol: FCDD-CBO-OP Email: raymond.a.diberardo.civ@mail.mil Phone: 410-436-3103



This research was developed with funding from the Defense Advanced Research Projects Agency (DARPA). The views, opinions and/or findings expressed are those of the author and should not be interpreted as representing the official views or policies of the Department of Defense or the U.S. Government.

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